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Mercury and SO_3 Emissions in Oxy-Fuel Combustion

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Abstract

This paper presents results on experiments carried out at a 20 kW combustion rig simulating different extents of oxy-fuel recycle gas cleaning by impurities injection to the oxidant gas of the once-through combustion reactor. A comprehensive set of total (Hg^{tot}), elemental (Hg^0) and oxidized (Hg^{2+}) mercury as well as SO_3 concentrations was obtained before and after the combustion rig's baghouse filter for in total 14 air and oxy-fuel experiments with 3 Australian coals. Based on this data, an assessment in respect to Hg oxidation, SO_2/SO_3 conversion and Hg and SO_3 capture on the test rig's filter was performed. The air and the oxy-fuel experiments with different extents of recycle gas cleaning, revealed differences in the Hg and SO_3 formation and capture behavior: The Hg^{2+}/Hg^{tot} ratios in the flue gas are higher during oxy-fuel combustion compared to air-firing. This effect is even more pronounced at the filter outlet, after flue gas has passed through the filter ash. In some experiments, even a net oxidation of Hg^0 entering the filter to Hg^{2+} was observed. The Hg capture by ash in the baghouse filter has been found to reduce the Hg emissions considerably. However, the Hg capture was altered by the different oxy-fuel recycle configurations, leading to decreased Hg capture efficiencies on the filter for one of the coals. A coal-specific trend of increased SO_2/SO_3 conversion ratios with increased flue gas SO_2 levels was observed that could be related to the ash composition of the three different coals. This and the higher SO_2 concentrations in the flue gas lead to considerably higher SO_3 levels in oxy-fuel combustion with SO_2 recycling. During the experiments, also a considerable capture of SO_3 in the baghouse filter was observed (up to 80% under air- and up to 66% under oxy-fired conditions). A reduction of the SO_3 capture on the filter under oxy-fuel conditions may be related to the higher SO_3 levels in this process.

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Keywords: Oxy-fuel combustion; Hg; mercury emission; mercury oxidation; mercury speciation; mercury capture; SO_x; sulfur trioxide; SO_3; sulfuric acid; H_2SO_4

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1. Introduction and background

1.1. Oxy-fuel combustion

To reduce the impact of anthropogenic greenhouse gas emissions on the earth's climate, CO_2 capture and storage/utilization (CCS, CCU) technologies for coal-fired power generation were developed to concentrate the CO_2 for processing and sequestration/utilization. Oxy-fuel combustion is one of these CCS/CCU technologies. In oxy-fuel operation, coal is burned with a mixture of O_2 and recirculated flue gas, instead of air. The mixing of O_2 with recirculated flue gas is, among other issues, necessary to lower the temperature in the furnace which otherwise would exceed the limits of construction materials of the boiler [1]. Due to the lack of flue gas dilution by airborne N_2, the concentrations of flue gas components such as CO_2, SO_2 and H_2O under oxy-fuel-fired conditions generally increase considerably by a factor of around 4 [1–3]. Moreover, under oxy-fuel-fired combustion conditions higher Hg concentrations than in air-firing are expected. NO_x formation is also altered, being affected by O_2 injection conditions, burner configurations and airborne N_2 exclusion from the combustion [4]. SO_3 that is formed by an oxidation of SO_2, is known to be responsible for low temperature corrosion in cold parts of the flue gas train (e.g. air preheater, recycle lines), while the acid gases NO_x and SO_x together with condensed water form highly acidic and therefore corrosive liquids in the CO_2 compression system. The higher Hg concentrations in an oxy-fuel process have potential implications on environmental pollution as well as on corrosion of Al-alloys by Hg [5]. This Al corrosion can be particularly problematic in the CO_2 processing unit of an oxy-fuel plant, where Al-alloys are applied e.g. for heat exchangers.

Various oxy-fuel process configurations (wet/dry recycle, environmental control units) as well as process conditions (recycle rate, residence time and thermal profile) are possible and have a significant impact on the concentrations and reactions of impurities, such as SO_x and Hg [6, 7]. To minimize corrosive material attack and subsequent safety risks, these impurities must be controlled. However, the choice of control units will affect achievable reduction efficiencies and ultimately also plant costs and waste streams.

The performed experiments aim to show how different fuels and different oxy-fuel process configurations impact the SO_3, Hg^0 and Hg^{2+} concentrations in the flue gas and the SO_3 and Hg removal on a baghouse filter. Injection of impurities to the oxidant gas was used to simulate recycle concentrations of impurities without adversely affecting the reactor configuration. Using this method, it was possible to provide gas concentrations comparable to both fully cleaned "cold" recycle conditions and "hot recycle" impurity levels associated with limited/practical flue gas cleaning. A detailed description and assessment of the underlying experiments has been previously published in two articles by Spörl et al. [8, 9] (Reprinted in part with permission from [8, 9], Copyright 2014 American Chemical Society.). This paper aims to coherently summarize the main results of both those articles.

1.2. Hg^0 and Hg^{2+} generation and capture

Mercury occurs in coals mostly associated with sulfur compounds (e.g.: FeS_2) or organic fractions [10–13]. During combustion Hg is completely evaporated and converted to its elemental form Hg^0 [14], reaching Hg concentrations in a range of 1-20 $\mu g/m^3$ in air-fired systems [15]. During cooling of the flue gases and via the interactions with other flue gas compounds (most importantly Cl-containing species) Hg^0 becomes oxidized to Hg^{2+} (e.g. in form of $HgCl_2$) [11, 14–17]. The most important factors influencing the concentration levels, speciation and removal of Hg from flue gas are:

- Hg content of coal
- Cl (and Br) content of coal
- Combustion conditions
- SO_x concentrations and speciation
- Fly ash properties (UBC, Ca, catalytically active compounds)
- Temperature-residence time profile of the plant

- Application of gas cleaning equipment (SCR, FGD, filters, sorbent injection)

The Hg oxidation reaction sequence is complex and different Cl-containing gas species such as Cl, Cl_2 and HCl impact the Hg oxidation differently [11, 14, 18, 19]. Higher Cl contents in the fuel can lead to higher Hg oxidation [11]. Besides the homogenous pathway, Hg oxidation can also occur via heterogeneous reactions, e.g. on fly ash [11, 14, 20], injected activated carbon [11, 16] or on SCR catalysts [10, 11, 13, 16, 21]. Heterogeneous Hg oxidation can occur on entrained fly ash as well as on ash deposited on filters [12, 22, 23]. The Hg^0/Hg^{2+} conversion in coal fired systems, is not complete, but kinetically limited [11, 13] and depends on the availability of Cl (and Br) and catalytically active materials. Hg^0/Hg^{2+} conversion also depends on factors such as combustion conditions (e.g. combustion stoichiometry) and temperature profile/quench rate of the flue gas (e.g. plant load) [14, 24]. SO_2 and SO_3 in the flue gas may influence the availability of Cl radicals and reduce the catalytic activity of fly ash for the Hg oxidation [11, 12], so that high S coals can show low Hg oxidation, even if the coals are high in Cl. However, according to Kellie et al. [25] SO_2 may also encourage Hg oxidation.

Hg capture/sorption on fly ash benefits from high unburned carbon (UBC) contents in the ash [13, 14, 20, 26–28]. However, not only the UBC content of the ash but also its structure is important for Hg capture/sorption [14, 20]. Hg may also be adsorbed on inorganic fly ash components or purposely added mineral based sorbents [14]. Its removal by the ash in filters decreases with increasing temperatures [13, 21, 29]. High filter ash loadings may improve the Hg capture on filters [30]. Direct capture of Hg^0 on fly ash is believed to be of minor importance, while the sorption of Hg^{2+} or of Hg^0 with subsequent oxidation to Hg^{2+} and capture of the oxidized Hg on the surface seems to be more important for the Hg removal in filters [23]. If only little carbon or other sorption sites are available on the ash or available sorption sites are consumed by Hg^{2+} or sulfur species (e.g. SO_3), the chlorinated Hg generated on the ash may desorb and lead to an overall oxidation of gas phase Hg without significant Hg removal [11, 23, 26]. The Hg oxidation on fly ash can be promoted by acid gases such as HCl, SO_2 or H_2SO_4 [14, 27, 31], while increased SO_3/H_2SO_4 are reported to decrease the potential for sorption of Hg^{2+}, since both species adsorb on the same sorption sites on carbon surfaces [11, 13, 16, 32, 33]. Also Ca in the ash can impact Hg oxidation and capture. Ca in the ash may reduce the availability of Cl in the gas phase and therefore Hg oxidation [34], but also may offer sorption sites for chlorinated Hg [26]. Moreover, the poisoning effect of SO_3/H_2SO_4 on Hg sorption may be beneficially affected by Ca or alkalis in the ash that can absorb SO_3/H_2SO_4 [16, 23, 33].

Besides in baghouse filter systems, Hg removal can take place in ESPs, FGDs and can be promoted by activated carbon injection [21, 35]. Removal efficiencies of Hg in flue gas cleaning equipment are affected by factors such as Cl and S content of coal, composition of ash (e.g. UBC), degree of Hg oxidation at the cleaning equipment inlet and type and operation mode of the applied flue gas cleaning equipment [13, 21, 22]. As shown by Pavlish et al. [35] the scatter of reported Hg removal efficiencies in different flue gas cleaning unit operations is high and significantly affected by the used coal types. For example, baghouse filter systems in bituminous coal fired systems typically can be expected to remove between 40 and 90% of the Hg in the flue gas [35].

For oxy-fuel combustion, only limited information on the Hg emission behavior is available. The impact of the change from an N_2 to a CO_2 atmosphere was shown to have no considerable impact on equilibrium behavior of Hg [36]. The Hg speciation and capture in oxy-fuel systems can be impacted by the increase of the H_2O, HCl, SO_x and Hg concentrations in the flue gas and by a change in NO_x concentrations (caused by the absence of air-borne N_2 in oxy-fuel operation) [35]. Oxy-fuel combustion in pilot scale showed a doubling [7] or tripling [29] of Hg levels in the flue gas compared to air-firing. Changes in the HCl, SO_x and Hg concentrations can improve Hg oxidation, but may also decrease Hg capture and depend on the kind and extent of recycle gas cleaning in an oxy-fuel system [35]. Altered ash loadings and changes in the temperature profile in an oxy-fuel combustion process can also affect Hg oxidation and capture [35]. Moreover, the increased residence time of flue gases that are partially recycled and therefore pass flue gas cleaning equipment several times can improve the Hg emission behavior [37].

1.3. SO_3 generation and capture

During combustion and along the flue gas path, SO_3 is formed from SO_2 in a homogeneous gas phase reaction or in a heterogeneous, solids catalyzed reaction for example on iron oxides [38, 39]. The following parameters have generally a significant influence on the concentrations of SO_3:

- Sulfur content of coal (SO_2 partial pressure)
- Alkaline/earth-alkaline content of the ash
- Oxygen partial pressure
- Content of catalytically active compounds in the ash (e.g. Fe_2O_3)
- Temperature-residence time profile of the plant
- Application of gas cleaning equipment (SCR, FGD, filters, sorbent injection)

The sulfur content of the coal affects directly the SO_2 partial pressure and therefore indirectly the SO_3 levels and is one of the most important parameters influencing the SO_3 concentrations in the flue gas, with higher sulfur contents leading to higher SO_2 and therefore SO_3 levels [40]. Another important parameter is the content of alkaline and earth-alkaline compounds in the ash, since they can capture SO_3 from the flue gas, forming sulfates. Also a reduction of SO_2 levels via SO_2 capture by alkalis and earth-alkalis impacts SO_3 levels. SO_3/H_2SO_4 in the flue gas is also effectively reduced by adsorption or by condensation on fly ash particles at temperatures near to or below the sulfuric acid dew point (ADP) temperature [41], e.g. in filters. The SO_3 formation in the boiler and down to approx. 500°C is influenced by the presence and amount of catalytically active compounds in the ash (e.g. Fe_2O_3) [39]. Catalytic SO_3 formation is highly temperature dependent, with a maximum of the SO_2/SO_3 conversion at about 700°C [42]. The homogeneous, just as the catalytic SO_3 formation, also shows a temperature-dependent behavior [40]. Both are relatively slow [39], which is the reason why in technical firing systems, no equilibrium concentrations of SO_3 can be observed. Therefore, the temperature-residence-time-profile of the flue gas in a plant is another key parameter influencing the formation of SO_3 [38, 40]. Also, the O_2 concentration in the flue gas has a effect on the SO_3 formation rate, which increases with increasing O_2 contents [36, 40]. Besides the above mentioned fuel properties and operating parameters, installed flue gas cleaning equipment has a considerable impact on SO_3 concentrations. For example, 0.5-2 % of the SO2 can be catalytically oxidized to SO_3 in SCR $DeNO_x$ systems, leading to increased SO_3 concentrations [39, 41]. In flue gas cleaning systems, such as FGDs, ESPs, baghouse filters or by injection of sorbents, SO_3 concentrations can be reduced considerably [38]. In practice, SO_2/SO_3 conversion efficiencies between 1 and 5% [43] with SO_3 concentrations up to about 40 ppm in coal fired air and over 180 ppm in oxy-fuel facilities were reported [44, 45]. However, in a comprehensive study by Fleig et al. [40], no clear trend was observed on changes in the SO_2/SO_3 conversion efficiencies between air and oxy-firing.

At temperatures below about 400°C gaseous sulfuric acid (H_2SO_4) starts to form from the reaction of SO_3 and water vapor and reaches complete transformation at approximately 200°C [46, 47]. The acid dew point of the formed H_2SO_4 depends on the concentrations of H_2O and SO_3/H_2SO_4 in the flue gas. It can be calculated based on those species' partial pressures according to empirical equations proposed by Verhoff and Banchero [48], Okkes [49] or more recently by ZareNehzhad [50]. In power plants, ADPs typically range between 95 and 160°C. With increased H_2O and SO_3/H_2SO_4 concentrations in oxy-fuel operation, considerably higher ADPs can be found. When temperature falls below the ADP, gaseous H_2SO_4 starts to condense. In power plants, relevant temperatures are found in the region of filters/precipitators and air pre-heaters, where substantial problems due to low temperature corrosion can occur [50]. In oxy-fuel plants, also the recycle lines are critical in respect to low temperature H_2SO_4 corrosion. Generally the air/oxidant pre-heater outlet temperature is limited to temperatures above the acid dew point of the flue gas, which limits the utilization of the flue gases' sensible heat and thereby lowers a plant's efficiency. In cold parts of power plants, also fouling by sulfate deposits can be a severe problem triggered by SO_3/H_2SO_4.

2. Experimental

2.1. Experimental combustion rig

Experiments were carried out at a 20 kW_{th} electrically heated once-through combustion rig (Fig. 1) at the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Germany. The electrically heated furnace (length: 2.5 m; diameter: 0.2 m) was operated at a wall temperature of 1350°C, with a constant gas product rate of about 11.5 m^3 (STP)/h to maintain comparable gas residence times in the system for all experimental settings. After the furnace, flue gases were drawn through an electrically heated flue gas duct, in which the gas temperature drops from approx. 700 to 200°C in about 4s. Flue gas enters the heated baghouse filter at gas temperatures of approx. 225°C (+/-30 °C) and exits at about 195°C (+/-15 °C).

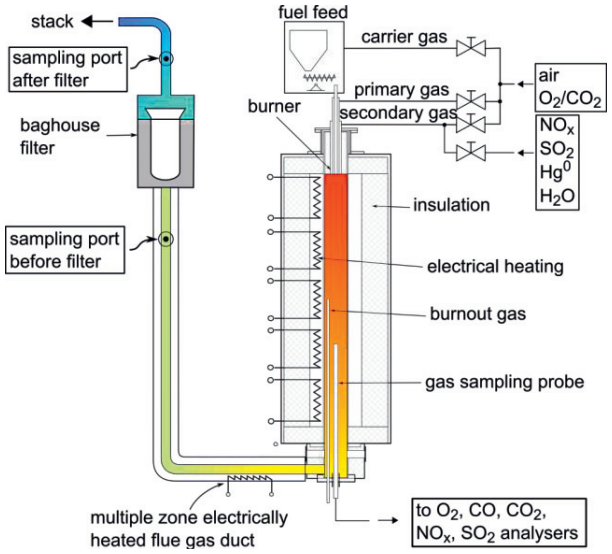

Fig. 1. Schematic of the experimental combustion rig used for air and oxy-fuel investigations (Reprinted with permission from [8, 9], Copyright 2014 American Chemical Society.)

In the air-firing mode, the combustion rig's top-mounted burner is fed with cleaned and dried air, whilst a mix of CO_2 and O_2 is fed to simulate flue gas recycling under oxy-fuel operation. In this way, oxy-fuel recycle rates can be adjusted by the O_2 concentration in the oxidant. To simulate the flue gas recycle of an oxy-fuel process with impurities present in the recycled gas, the oxidant gas can be doped with desired amounts of NO_x, SO_2, Hg^0 and H_2O. For the doping of Hg, a Hg^0 vapor generator was used that was described previously [8]. This method allows for an investigation of oxy-fuel combustion simulating different extents of recycle gas treatment (e.g. varying Hg^0 and SO_2 removal rates).

To evaluate Hg oxidation and the removal of Hg and SO_3 in the filter, comprehensive SO_3, Hg^0 and Hg^{2+} measurements were performed before and after the rig's filter. During the experiments, the filter was cleaned regularly to counteract a drop in the flue gas flow rate and therefore in the flue gas residence time in the system. To accomplish minimum possible differences of the ash loadings on the filter, even though the fuels used had considerably differing ash contents, the filter was cleaned before each Hg or SO_3 sampling was started. During the course of an individual measurement, the filter cleaning was discontinued.

2.2. Measurement and sampling equipment and procedures

During the performed experiments, the gases O_2, CO_2, SO_2, NO_x and CO were continuously sampled with a tempered (~180°C) sampling probe at the end of the furnace and analyzed (details on applied analyzers and calibration gases can be found in [8, 9]). Reported H_2O concentrations were calculated, based on coal composition and water injection. HCl concentrations were measured applying standards DIN EN 1911 [51] and DIN EN ISO 10304 [52]. Coals were analyzed for their calorific value (DIN 51900 [53]), proximate (DIN 51734 [54], DIN 51718 [55], DIN 51719 [56], DIN 51720 [57]) and elemental (DIN 51732 [58], DIN 51724 [59], DIN 51733 [60]) composition, Cl (DIN 51727 [61]) and Hg (DIN 22022 [62]) contents and ash composition (DIN 51729 [63]). In all experiments, ash samples were extracted at the end of the furnace and from the combustion rig's filter and were analyzed for their C in ash, S and main ash forming elements' contents (according to standards DIN 51732 [58], DIN 51724 [59] and DIN 51729 [63]).

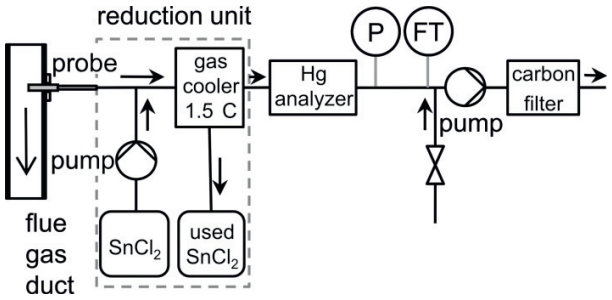

Fig. 2. Schematic of the Hg sampling train (Reprinted with permission from [8, 9], Copyright 2014 American Chemical Society.)

Measurements of elemental and total Hg in gas phase (Hg^0 and Hg^{tot}) were performed before and after the baghouse filter of the combustion rig using a continuous RA-915M Hg analyzer by Lumex Ltd. that measures Hg^0 based a cold-vapor atomic absorption at 253.7 nm. Since the analyzer is only capable of measuring elemental Hg^0, a sample gas conditioning system was applied to convert oxidized forms of Hg to Hg^0 by contacting the gas with an aqueous $SnCl_2$ reduction solution. In this configuration, with a Hg^{2+} reduction unit upstream the Hg^0 analyzer, the system measures the total concentration of Hg ($Hg^{tot} = Hg^0 + Hg^{2+}$). A schematic of the sampling train for measuring Hg^{tot} is shown in Fig. 2. For measurements of elemental Hg (Hg^0), the sampling train was equipped with an additional Hg^{2+} trap (as proposed by Metzger and Braun [64]) to knock out $HgCl_2$ selectively and quantitatively after the probe and before entering the Hg^{2+} reduction system. From the measured concentrations of Hg^0 and Hg^{tot}, the concentration of Hg^{2+} was calculated: $Hg^{2+} = Hg^{tot} - Hg^0$. Reported Hg^0 and Hg^{2+} concentrations represent averaged concentrations from an interval of approx. 5-10 minutes of stable and representative Hg measurement. A more detailed description of the applied Hg measuring equipment and procedures was published previously [8].

During the experiments, SO_3 concentrations on dry basis were measured before and after the combustion rig's filter based on the standard VDI 2462 [65] (controlled condensation method) with ion chromatographic sample analysis (DIN EN ISO 10304 [52]). Relevant sections of the flue gas duct and the sampling probe and filter were heated above the ADP to avoid premature condensation of H_2SO_4 during sampling which would lead to a negative bias in measurements. Reported SO_3 measurements are mean values, calculated from 3 single measurements. When measuring SO_3 and Hg, fly ash was separated from the sample gas by an in-stack filter. This filter was changed in between single samplings to minimize the impact of filter ash on the measurements. All Hg and SO_3 concentrations reported in this article are related to standard conditions (DIN 1343 [66]: 0°C, 1 atm).

2.3. Coal properties

The three Australian coals (A, B and C) used in this study were shipped from Australia to IFK and then prepared and crushed for the experiments. Coal properties are listed in tables 1 and 2. The coals differ considerably in their ash, mercury and sulfur contents. The ash contents of coals A, B and C are in a proportion of roughly 3:2:1, while the Hg contents are in a proportion of 3.5:2:1 and the S contents are in a proportion of about 1:2:2, respectively. The Cl contents of all three coals are low, with coal C having the highest Cl content of 0.017 wt.%. When Fe contents referring to raw coals are calculated, coal A has the highest content with 1.55 wt.%, followed by coals C and B with contents of 0.3 wt.% and 0.09 wt.%, respectively. The high ash coals A and B are rich in Al and Si, but relatively low in alkaline and earth alkaline elements (Ca, Mg, K, and Na). In contrast, coal C contains considerably higher contents of those elements. The lower alkaline and earth-alkaline content of coal A however is compensated by this coals high ash content so that this coals molar (Ca+Mg)/S as well as its (K+Na)/2S ratios are higher than that of coal C, indicating a higher sulfur retention potential. Coal B has the lowest molar (Ca+Mg)/S and (K+Na)/2S ratios of all 3 tested coals.

Table 1. Net calorific value (NCV), proximate, elemental, Cl and Hg analyses of the investigated Australian coals [percentages on a weight basis; W: water; A: ash; V: volatiles; FC: fixed carbon; n.d.: not determinable (< 0.008 %, daf); oxygen calculated by difference] (Reprinted with permission from [8, 9], Copyright 2014 American Chemical Society.)

Coal	NCV [kJ/kg]	W [%, ad]	A [%, db]	V [%, daf]	FC [%, daf]	C [%, daf]	H [%, daf]	N [%, daf]	S [%, daf]	O [%, daf]	Cl [%, daf]	Hg [mg/kg, daf]
A	18026	3.9	32.5	35.9	64.1	73.8	4.3	1.1	0.3	20.5	n.d.	0.07
B	24956	1.5	23.0	50.6	49.4	78.3	6.7	1.1	0.7	13.2	0.014	0.04
C	26748	3.7	9.8	35.9	64.1	77.2	5.2	2.0	0.7	15.0	0.017	0.02

Table 2. Analysis of coals by ICP-OES for main ash forming elements [Differing to the DIN 51729 standard for ICP-OES analysis of fuels, the coal samples were analyzed without previous ashing at 815°C, to ensure a quantitative analysis of highly volatile ash compounds (e.g. K, Na)] (Reprinted with permission from [8, 9], Copyright 2014 American Chemical Society.)

Coal	SiO_2 [wt.%]	Al_2O_3 [wt.%]	Fe_2O_3 [wt.%]	CaO [wt.%]	MgO [wt.%]	SO_3 [wt.%]	K_2O [wt.%]	Na_2O [wt.%]	TiO_2 [wt.%]	P_2O_5 [wt.%]
A	58.9	26.2	6.8	1.2	0.7	3.0	0.4	0.1	2.4	0.2
B	64.4	21.5	1.2	0.4	0.7	7.2	0.4	0.2	3.9	0.0
C	33.2	23.0	11.4	7.0	1.8	22.7	0.9	1.3	1.2	1.8

2.4. Combustion Conditions

The investigated combustion conditions include conventional air-firing and a number of simulated oxy-fuel atmospheres with flue gas recycling: Combustion in a pure CO_2/O_2 atmosphere as well as 6 different CO_2/O_2 atmospheres with additional injection of impurities (H_2O, NO, SO_2 and Hg^0) were tested. By variation of the impurity injection rate, different impurity removal extents from the recycled gas were simulated. Table 3 lists all experimental settings including simulated removal rates in detail. The removal rates refer to calculated, theoretical concentration maxima for H_2O, SO_2 and Hg in an oxy-fuel process without any impurity removal and an exit O_2 concentration of 3 Vol.-% (dry). This experimental approach was described in detail elsewhere [8, 9].

Table 3. List of all experimental settings and simulated removal rates (Reprinted with permission from [8, 9], Copyright 2014 American Chemical Society.)

Index	Coal	air/oxy	Simulated capture rates [%]			Simulated NO conc. in rec. flue gas [ppm, dry]
			H_2O	SO_2	Hg	
A-A		air	-	-	-	-
A-OC		Oxy28 - clean	100	100	100	-
A-O2S5H	A	Oxy28	23	23	44	962
A-O5S5H		Oxy28	23	52	44	962
A-O2S8H		Oxy28	23	23	79	962

A-O0S5H		Oxy28	23	4	44	962
A-O2S0H		Oxy28	23	23	7	962
A-O0S0H		Oxy28	23	4	7	962
B-A		air	-	-	-	-
B-OC	B	Oxy28 - clean	100	100	100	-
B-O2S5H		Oxy28	24	24	51	949
C-A		air	-	-	-	-
C-OC	C	Oxy28 - clean	100	100	100	-
C-O2S5H		Oxy28	23	23	62	959

The experiment with pure O_2/CO_2 combustion (i.e.: removal of 100 % of all impurities) can be considered as a "clean oxy-fuel" configuration (labelled as OC). In the other oxy-fuel experiments, the H_2O removal rate was fixed at approx. 20% and a constant concentration of NO (approx. 1000 ppm) in the recycled flue gas was simulated. SO_2 removal rates of approx. 50%, 20% and 0% and Hg removal rates of approx. 80%, 50% and 0% were tested. Slight deviations from the desired removal rates can be observed, but experiments with different coals and similar removal rates are considered comparable. All experiments are labelled with a code, allowing for identification of the experimental setting: e.g.: C-O2S5H indicates an experiment with coal C (index: C) under oxy-fuel conditions (index: O) with simulated removal of 20% of the SO_2 (index: 2S) and 50% of the Hg (index: 5H). Coals A, B and C were tested under A, OC and O2S5H conditions and coal A was investigated with 5 additional oxy-fuel configurations. In the oxy-fuel experiments the oxidant's O_2 concentration was fixed at 28 Vol.-% (wet), which corresponds to recycle rates of about 70%.

3. Results and discussion

3.1. Flue gas composition

Table 4 lists the measured/calculated concentrations of O_2, SO_2, H_2O and HCl. The concentrations of O_2 and SO_2 that were measured at the furnace exit, represent mean values, calculated based on minimum 10 minutes of stable, representative operation. The O_2 concentrations were kept relatively stable around 3 Vol.-% (2.8-3.6 Vol.-%, dry). During all oxy-fuel experiments, CO_2 concentrations higher than 95 Vol.-% (dry) were reached, proving a minimum amount of air ingress to the system. All mean CO concentrations were below 90 ppm (< 25 ppm in most cases). Different fuel sulfur contents and different fuel feed rates between air (A) and oxy-clean (OC) combustion are directly represented in differences in the measured concentrations of SO_2. HCl concentrations during all experiments are low (<10 ppm), as expected based on the low Cl content of the coals.

Table 4. O_2 and SO_2 concentrations measured at end of furnace, H_2O concentrations calculated based on fuel composition and steam injection to the oxidant gas and HCl concentrations measured before filter (Adapted with permission from [8, 9], Copyright 2014 American Chemical Society.)

Index	**A-A**	**A-OC**	**A-O2S8H**	**A-O5S5H**	**A-O2S5H**	**A-O0S5H**	**A-O2S0H**	**A-O0S0H**	**B-A**	**B-OC**	**B-O2S5H**	**C-A**	**C-OC**	**C-O2S5H**
O_2 [Vol-%, dry]	3.0	3.4	3.0	3.1	3.6	3.2	2.7	2.9	3.1	3.2	3.0	3.1	2.8	3.1
H_2O [Vol-%, wet]	6.4	8.7	23.5	23.5	23.5	23.5	23.5	23.5	7.6	10.4	28.5	6.6	9.1	24.3
SO_2 [ppm, dry]	199	283	1228	871	1235	1464	1243	1531	367	498	2578	444	603	2802
HCl [ppm, dry]	4	3	4	4	4	4	4	4	3	5	7	6	8	9

3.2. Composition of ash samples

The UBC contents of all baghouse filter ashes involving coal C were low (0.1-0.75%) and those from coal A and B were below the detection limit of 0.1%. This illustrates that all UBC contents were at similar, low levels and that

the influence of variations in the UBC content on the measured Hg and SO_3 concentrations may be limited. Hg and S contents of the ash were close to or below the detection limit.

3.3. Hg concentrations, speciation and capture

Figure 3 shows concentrations of Hg^0 and Hg^{2+} measured before and after the baghouse filter as well as the theoretically possible maximum Hg^{tot} concentrations for all performed air and oxy-fuel experiments. The results for each coal are ordered in the range from high to low Hg removal rates (and from low to high oxidant Hg^0 concentrations) from left to right. One sees that theoretically calculated Hg^{tot} concentrations match well with Hg^{tot} concentrations measured in the flue gas before filter indicating that fly ash on the in-stack sample gas filter at temperatures greater than approx. 350°C does not capture Hg and therefore has no influence on the measured Hg^{tot} levels. Hg measurements after filter should also not be influenced by fly ash, since the flue gas is practically ash free at this location. Differences in the measured Hg concentrations can be observed, that were expected based on the differences of the coals' Hg contents, with coal A having the highest and coal C having the lowest Hg emissions. When comparing the combustion conditions, one observes that not only the oxy-fuel settings with Hg doping to the oxidant gas, but also the clean oxy-fuel experiments (Index "OC") show higher Hg^{tot} concentrations than the air combustion. The reason for this is that the higher oxidant O_2 in the clean oxy-fuel experiment (28 Vol.-%) requires a higher fuel feed. This effect can also be found in the measured SO_2 concentrations presented in table 5. In figure 3 the impact of simulated Hg recycle on measured Hg concentrations is obvious. For example, the oxy-fuel combustion test without any Hg removal (A-O0S0H) from recirculated flue gas leads to a 3.3 fold increase in the Hg concentrations before filter and a 4.5 fold increase after filter, compared to a recycle configuration with complete removal of Hg (A-OC). Even though, Hg concentrations are higher under oxy-fired conditions, energy based Hg emission [i.e.: mg Hg/MJ] are similar or lower than in air-firing.

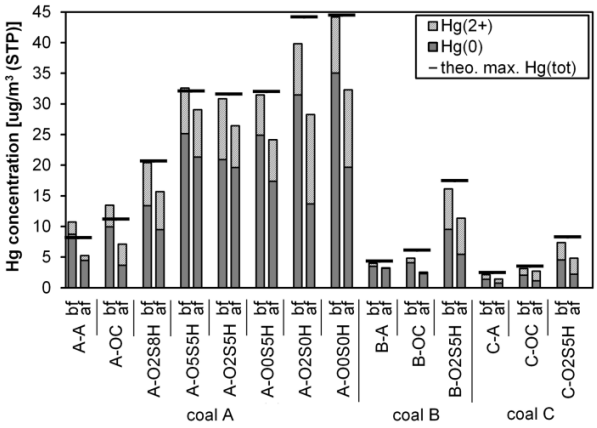

Fig. 3. Hg^0 (solid) and Hg^{2+} (hatched) concentrations measured before (bf) and after (af) filter and theoretically calculated maximum concentrations for air and oxy-fuel experiments with coals A, B and C (Adapted with permission from [8], Copyright 2014 American Chemical Society.)

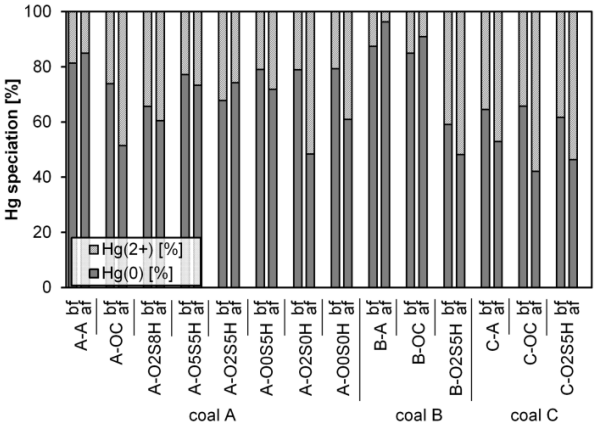

Fig. 4. Percentaged speciation between Hg^0 (solid), Hg^{2+} (hatched) before (bf) and after (af) filter for coal A, B and C experiments (Adapted with permission from [8], Copyright 2014 American Chemical Society.)

In Figure 4 the percentaged speciation between Hg^0 and Hg^{2+} of the measured Hg^{tot} before and after filter for air, clean oxy-fuel and oxy-fuel experiments with impurity recycling is shown for all 3 coals. One observes for all coals that a switch from air to oxy-fuel combustion with impurity recycling leads to an increased Hg^{2+}/Hg^{tot} ratio at the sampling locations before and after filter. Moreover, in almost all experiments with relatively high proportions of Hg^{2+} (> 25%) before filter, this proportion is even increasing, when flue gases pass the filter. In contrast, in all experiments with low proportions of Hg^{2+} (< 25%) before filter, Hg^{2+} proportions are decreasing. An improvement

of the homogenous and/or heterogeneous Hg oxidation on fly ash by SO_2 and/or SO_3/H_2SO_4 may explain the increased Hg oxidation under oxy-fuel combustion conditions with impurity recycling compared to air-firing. Possible effects of SO_2 and SO_3/H_2SO_4 on Hg oxidation were discussed by others [14, 25, 27, 31].

In all performed experiments one observes lower Hg^{tot} concentrations at the filter outlet than at the inlet, due to Hg capture on the ash in the filter (see Fig. 3). Based on Hg concentrations measured before and after filter, Hg capture efficiencies were calculated according to equation (1):

$$\eta_{\mathrm{Hg,l}} = \frac{c_{\mathrm{Hg,l,bf}} - c_{\mathrm{Hg,l,af}}}{c_{\mathrm{Hg,tot,bf}}} * 100\% \quad (1)$$

In Figure 5 the Hg^0, Hg^{2+} and Hg^{tot} capture efficiencies for all performed experiments are shown. Considerable Hg^{tot} capture on the baghouse filter was observed with capture efficiencies between 18 and 51% for air (A), between 13 and 47% for oxy-clean (OC) and between 10 and 34% for oxy-fuel combustion with impurity recycling (i.e. O2S5H experiments). The reduction of Hg^{tot} capture efficiencies in the coal A oxy-fuel experiments with impurity recycling compared to air and oxy-clean experiments may be connected to the relatively high Hg^{tot} concentrations at the filter inlet in those experiments. Also higher SO_2 and SO_3 concentrations that can lead to a depletion of Hg sorption sites may be involved in the capture efficiency decrease. However, the Hg^{tot} capture efficiencies in coal A experiments with impurity recycling and therefore considerably higher SO_3 concentrations compared to the air and oxy-clean experiments show a positive correlation between SO_3 levels at the filter inlet and Hg^{tot} capture. Considering the low unburned carbon content of filter ashes of this high-ash coal, possibly for coal A not only carbon sorption sites play a role in the Hg capture, but also mineral species [14, 67]. The Hg^{tot} capture on ash may also profit from the improved Hg oxidation at higher SO_3/H_2SO_4 levels [14, 27] and from an acidification of the ash [67, 68].

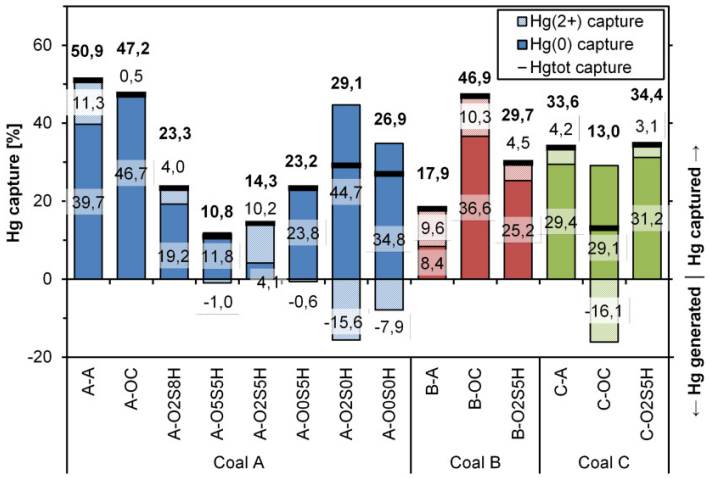

Fig. 5. Hg^0 (solid), Hg^{2+} (hatched) and Hg^{tot} (black line & bold print) capture in the baghouse filter for coal A, B and C experiments (Adapted with permission from [8], Copyright 2014 American Chemical Society.)

Negative Hg^{2+} capture efficiencies at the baghouse filter were found for some experiments and can be interpreted as an overall Hg^0 oxidation at this unit, creating higher Hg^{2+} concentrations at the filter outlet than at the inlet. Such an effect was mainly observed for experiments with simulated Hg and SO_2 recycling and is at least partially responsible for the lowered Hg^{tot} capture efficiencies in these tests. Either a kinetic limitation of the Hg^{2+} chemisorption, a limited availability of sorption sites of coal A (low UBC, high SO_2 and SO_3) or a combination of

both can explain the behavior. In all cases, an increase of the availability of sorption sites for Hg^{2+} (e.g. by sorbent injection) may improve the Hg capture performance at the filter considerably.

3.4. SO_3 concentrations and capture

Figure 6 shows the SO_3 concentrations measured before and after the experimental rig's filter. The results for each coal are ordered in the range from high to low SO_2 removal rates (and from low to high oxidant SO_2 concentrations) from left to right. Before filter, increasing SO_3 concentrations can be observed when comparing settings lean in SO_2, such as "air" and "clean oxy-fuel" to the oxy-fuel settings with SO_2 recycling. As expected, in all experiments SO_3 is captured on the filter and concentrations after the filter are considerably lower than those before filter. For coals A and C barely any SO_3 was detected under air-fired conditions and coal C generated only measurable SO_3 concentrations in the oxy-fuel setting with SO_2 injection. Possibly, for those coals, a certain SO_2 level needs to be reached in order to generate measurable quantities of SO_3. The behavior is likely linked to the coals' ashes that provide high quantities of alkalis and earth-alkalis compared to coal B. At low SO_2 levels the generated SO_3 may efficiently be captured by the entrained fly ash, removing virtually all generated SO_3 from the gas. When SO_2 concentrations rise above a certain level, the ash becomes saturated or inactivated by sulfates so that SO_3 cannot be fully retained in the ash and therefore SO_3 can be found in the flue gas.

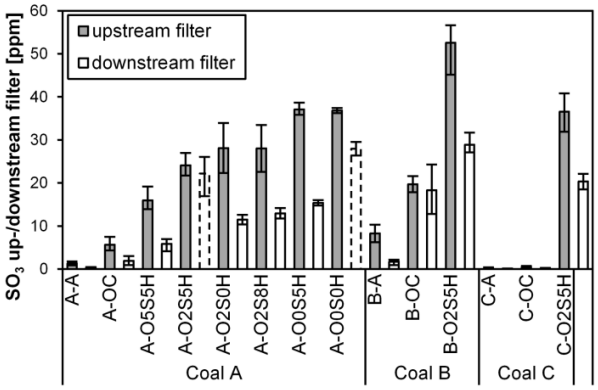

Fig. 6. SO_3 concentrations measured upstream and downstream filter (error bars indicate measured min. and max. concentrations) (Reprinted with permission from [9], Copyright 2014 American Chemical Society.).

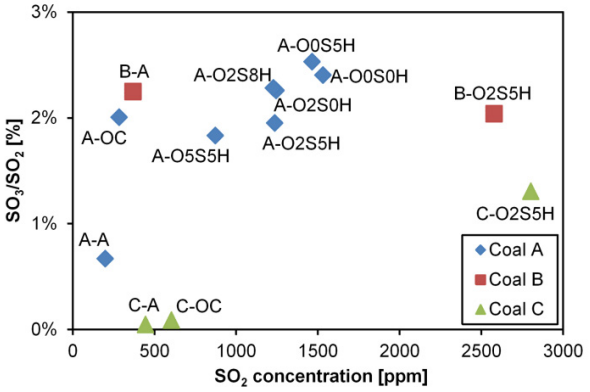

Fig. 7. Percentaged SO_2/SO_3 ratios upstream filter vs. SO_2 concentrations for air and oxy-fuel experiments with coals A, B and C (SO_2/SO_3 ratio for experiment B-OC = 3.95% is not shown here).

The observation of a coal-specific trend of increasing SO_2/SO_3 ratios with increasing SO_2 concentrations for coals A and C, but not for coal B (see Fig. 7) may also be associated with a saturation of the ash with sulfates leading to higher net SO_3 generation at higher SO_2 levels. For practical oxy-fuel applications such a coal-specific increase of SO_3/SO_2 ratios with increasing SO_2 may have the implication that coals which are unproblematic in respect to SO_3 formation under conventional air-fired conditions (e.g. low S, high Ca coals) may show an increased SO_3 generation in oxy-firing (without SO_2 removal from recycled gas), due to increase of SO_2 concentrations in such a process. Such an effect should be related to the content and reactivity of alkaline and earth-alkaline compounds in a coal's ash and likely will be not important for coals without considerable sulfur retention potential in their ash.

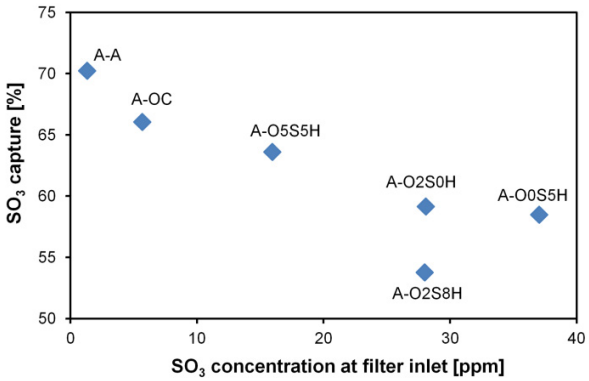

Fig. 8. . SO_3 capture efficiencies on the baghouse filter vs. SO_3 concentrations at the filter inlet for experiments with coal A (Reprinted with permission from [9], Copyright 2014 American Chemical Society.)

Based on the SO_3 concentrations measured before and after baghouse filter, the SO_3 capture efficiency of that unit was calculated according to equation (2):

$$\eta_{SO_3} = \frac{y_{SO_3,bf} - y_{SO_3,af}}{y_{SO_3,bf}} * 100\% \quad (2)$$

Under air-firing conditions SO_3 capture rates on the filter between 70 and 80% were observed (very low SO_3 concentrations considered). In most oxy-fuel experiments SO_3 capture rates between 44 and 66% were found. In figure 4, SO_3 capture rates for coal A tests are plotted versus SO_3 measured at the baghouse filter inlet. SO_3 capture rates at the filter decrease with increasing SO_3 concentrations at the filter inlet (and increasing SO_2 concentrations/decreasing SO_2 removal rates). This effect is possibly due to saturation of the filter ash for SO_3 capture, or by an insufficient residence time of the flue gas in the filter for capturing higher amounts of SO_3 and may be one explanation of the reduction of SO_3 capture efficiencies under oxy-fired conditions.

4. Summary and conclusion

A comprehensive study on Hg oxidation and capture and SO_3 formation and capture of three Australian coals under air and simulated oxy-fuel conditions with variable degrees of recycle gas cleaning was performed. The experiments highlight the importance of the fuels' Hg and S contents on the Hg and SO_2 concentrations in air and oxy-fuel combustion systems, since differences in the coals' Hg and S contents are directly represented by differences in the measured Hg and SO_2 concentrations. However, measured SO_3 levels in air and oxy-fuel operation were also considerably influenced by the coals' ash contents and compositions. Coal B that was very low in alkaline and earth-alkaline compounds generated the highest SO_3 levels under all tested combustion conditions (up to 52.5 ppm in experiments with SO_2 recycling). The experimental data also indicates a coal-specific trend of increasing SO_2/SO_3 conversion ratios with increased flue gas SO_2 levels that seems to be related to the ash composition of the combusted coals. For coal A that has high molar (Ca+Mg)/S and (K+Na)/2S ratios, SO_2/SO_3 conversion ratios were increased in experiments with SO_2 recycling and therefore high SO_2 levels in the flue gas (0.7% in air and 2 to 2.5% in oxy-fuel experiments with SO_2 recycling). For coal C that is relatively rich in Ca and Mg, only the experiment with SO_2 injection to the oxidant gas generated measurable amounts of SO_3, at a comparatively low SO_2/SO_3 conversion efficiency. A gradual saturation or inactivation these coals' ashes by sulfates that occurs when SO_2 concentrations rise above a certain level could explain these observations. Such a behavior would imply that coals which are unproblematic in respect to SO_3 formation under conventional air-fired conditions (e.g. low S, high Ca coals) may show an increased SO_3 generation under oxy-fired conditions (without sulfur removal from recycle gas)

due to the increased of SO_2 concentrations in such a process. The low alkali and earth-alkali coal B showed no increase of the SO_2/SO_3 conversion efficiency when switching from air to oxy-firing with SO_2 recycling (SO_2/SO_3 ratios: 2.2 and 2.0%, respectively).

The Hg^0 oxidation behavior of coals is also impacted when switching from air to oxy-fuel combustion with impurity recycling. For all three coals, increased Hg^{2+}/Hg^{tot} ratios at the sampling locations before and after filter were found under oxy-fired conditions. An absolute increase of the Hg^{2+}/Hg^{tot} ratio of up to 28% before filter and up to 48% after filter was found, when comparing oxy-firing with impurity recycling to air-firing. In most experiments the Hg^{2+} share and in some experiments also the Hg^{2+} amount increased when flue gas pass through the filter, indicating an oxidation of Hg^0 in this unit. The capture of Hg^{2+} formed in the filter may be limited by kinetics of the Hg^{2+} chemisorption on the ash and/or by the availability of Hg^{2+} sorption sites, leading to the increase of Hg^{2+}.

Under all experimental conditions, considerable amounts of Hg and SO_3 were captured when the flue gases passed through the filter. However, SO_3 capture efficiencies were lower in oxy-fuel experiments with impurity recycling compared to air-firing. The same observation was made in respect to Hg capture efficiencies of the filter for coal A. Possibly, higher SO_2 and SO_3 concentrations in the oxy-fuel experiments with impurity recycling are responsible for the reduced Hg capture efficiencies in those experiments. It was also observed that the extent of SO_3 capture on the filter reduced slightly with increasing SO_3 concentrations. This suggests of saturation behavior of the SO_3 capture mechanism on the filter.

Higher Hg and SO_3 concentrations and a decreased filter SO_3 capture and for some coals filter Hg capture performance in oxy-fuel combustion illustrate that a better understanding of Hg and SO_3 emission behavior, but more importantly suitable Hg and SO_3 control technologies are crucial in order to limit negative impacts of high Hg and SO_3 levels in oxy-fuel combustion processes (e.g.: low temperature H_2SO_4 corrosion in recycle lines, Al-corrosion by Hg in CO_2 liquefaction units). Higher levels of Hg oxidation, observed under oxy-fuel conditions with impurity recycling suggest that a greater portion of the total gas phase Hg can be removed during flue gas quenching prior to compression. Moreover, it is expected that further significant Hg removal would occur in a practical baghouse filter where UBC is higher than in the performed experiments. In addition, additive technologies that enhance the oxidation of gaseous Hg^0 and the capture of Hg and SO_3 on ash (e.g. activated carbon and $Ca(OH)_2$ injection) can ultimately reduce the amount of those impurities. On-going and future activities at IFK will further investigate the potential of such technologies under industrially relevant conditions.

Nomenclature

ad	air dried (fuel reference state)
db	dry basis (fuel reference state)
daf	dry, ash free (fuel reference state)
$\eta_{Hg,l}$	Percentaged Hg^0, Hg^{2+} or Hg^{tot} capture rate [%]
$c_{Hg,l,bf}$	Mass concentration of Hg^0, Hg^{2+} or Hg^{tot} before filter [µg/m^3 (STP)]
$c_{Hg,l,af}$	Mass concentration of Hg^0, Hg^{2+} or Hg^{tot} after filter [µg/m^3 (STP)]
l	Index indication the Hg speciation, e.g. Hg^0, Hg^{2+} or Hg^{tot}
η_{SO3}	Percentaged SO_3 capture rate in the filter [%]
$y_{SO3,\ i}$	Volumetric concentration in the flue gas [ppm, dry]
i	Index denoting sampling location: b.f. = before filter; a.f. = after filter
FGD	Flue gas desulfurization
$DeNO_x$	NO_x reduction
SCR	Selective catalytic (NO_x) reduction
ESP	Electrostatic precipitator
UBC	Unburned carbon
ADP	Acid dew point

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